

# Field Dependent Specific-Heat of Rare Earth Manganites

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## Abstract

The low temperature specific heat  $C(H)$  of several rare-earth manganites ( $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ,  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ,  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ,  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ,  $\text{La}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$  and  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ ) was measured as a function of magnetic field. We observed behaviour consistent with thermodynamic expectations, i.e.,  $C(H)$  decreases with field for ferromagnetic metallic compounds by an amount which is in quantitative agreement with spin wave theory. We also find that  $C(H)$  increases with field in most compounds with a charge-ordered antiferromagnetic ground state. In compounds which show evidence of a coexistence of ferromagnetic metallic and antiferromagnetic charge-ordered states,  $C(H)$  displays some unusual non-equilibrium effects presumably associated with the phase-separation of the two states. We also observe a large anomalous low temperature specific heat at the doping induced metal-insulator transition (at  $x = 0.50$ ) in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ .

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The rare-earth perovskite manganites,  $R_{1-x}A_x\text{MnO}_3$  (R and A are trivalent and divalent ions respectively) exhibit some intriguing features originating from the strong interplay between the electronic, magnetic and structural degrees of freedom. Recent studies have demonstrated that the [1] ground state of these materials can be changed by varying either the band-filling [2–4] or the band-width [5–7], and that the behaviour is extremely sensitive to the application of an external magnetic field leading to the so-called “colossal magnetoresistance”.

The stoichiometric manganites ( $\text{RMnO}_3$ ) are antiferromagnetic insulators [8,9], but the ground state of these materials can be tuned to a metallic ferromagnetic state by increasing the band filling [4]. At larger values of x, the ferromagnetic conducting state becomes unstable to a charge-ordered [10] antiferromagnetic ground state with large resistivity. For some values of x, the charge-ordered state can be dissociated by an external magnetic field, leading to a large magnetoresistance of many orders of magnitude. It has been recently demonstrated that there is a coexistence of phase-separated ferromagnetic metallic (FMM) and antiferromagnetic charge-ordered (ACO) states at both values of x near the cross-over between the two ground states, and also in the lower doping regime [11–21].

Measurements of specific heat provide insight into the nature of the excitations in these various phases and the phenomena responsible for the metal-insulator transitions. There have been a number of studies of the specific heat of the manganites, [22–27] but these studies primarily concentrated on the temperature dependence of the specific heat, and the contributions of different excitations to the specific heat were derived from analytical fits to the data. Since the field-dependent properties of these materials are responsible for much of the recent interest, we have performed a study of the field dependence of the low temperature  $C(H)$  on a range of manganite samples to elucidate how the thermodynamic properties of rare-earth manganites evolve as a function of magnetic field. We observe that the magnetic specific heat dominates the behaviour of  $C(H)$  and that the behaviour is typically consistent with simple thermodynamic expectations.

Specific heat was measured on both polycrystalline (pc) and single crystal (sc) man-

ganite samples. We studied two samples,  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (pc) and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (sc) with FMM ground states, three samples,  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (sc),  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (sc) and  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  (pc) with ACO ground states and two samples,  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  (pc) and  $\text{La}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$  (pc) which display strong evidence of a coexistence of FMM and ACO states. The single crystal samples were grown by floating-zone method, and the polycrystalline samples were synthesized by the solid-state reaction method. All our samples were single phase as adjudged by x-ray diffraction. Specific heat was measured by semi-adiabatic heat pulse method. All the samples were zero-field cooled to the prescribed temperature and the specific heat was measured as a function of field at a constant temperature in discrete steps of 0.25 T, as the field was swept from  $0 \rightarrow 9$  T,  $9$  T  $\rightarrow 0 \rightarrow -9$  T and  $-9$  T  $\rightarrow 0 \rightarrow 9$  T. Each step in field took a total of  $\sim 10$ -30 minutes, depending on the thermal mass of the samples, resulting in some non-equilibrium effects as discussed below. Moreover, the measured values of  $C(T)$  are in good agreement with those of previous studies [22–27].

From simple thermodynamics, one expects the field dependence of the magnetic contribution to the specific heat to be given by:

$$\left(\frac{\partial C}{\partial H}\right)_T \equiv T \left(\frac{\partial^2 M}{\partial T^2}\right)_H \quad (1)$$

For a ferromagnet in a positive field  $\frac{\partial^2 M}{\partial T^2} < 0$ , thus one expects  $\frac{\partial C}{\partial H} < 0$ , i.e.,  $C(H)$  decreases in a field. This can also be interpreted as the suppression of spin waves with increasing field. By contrast, for an antiferromagnet in a positive field,  $\frac{\partial^2 M}{\partial T^2} > 0 \implies \frac{\partial C}{\partial H} > 0$ , i.e.,  $C(H)$  increases with increasing field, which can alternately be viewed as the softening of the AFM order parameter in a field.

Figure 1 shows  $C(H)$  of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (sc) and  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (pc) at  $T = 5.45$  K. The specific heat of both samples decreases monotonically with increasing field, dropping by  $\sim 10$  % as the field is changed from 0 to 9T, although  $C(H)$  of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  is  $\sim 18\%$  higher, attributable to the larger lattice contribution due to the smaller size of Ca ion. The reduction in  $C(H)$  with increasing field can be explained as the suppression of thermal excitations of the spin waves as described above. Similar observations were also drawn from

the recent temperature dependent specific-heat experiments [28] on  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .

The magnon contributions to the specific heat of a ferromagnet in an external field neglecting any demagnetization effects, and assuming no spin gap at  $H = 0$ , so that the dispersion relation at an external field  $H$  is  $\omega = g\mu_B H + Dk^2$ , can be written as [29],

$$C_{\text{magnon}}(H) = \frac{k_B^{5/2} T^{3/2}}{4\pi^2 D^{3/2}} \int_{g\mu_B H/k_B T}^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} \sqrt{x - \frac{g\mu_B H}{k_B T}} dx \quad (2)$$

where  $x = (g\mu_B H + Dk^2)/k_B T$ , and  $D = 2JSa^2$  is the spin stiffness constant. We can thus calculate the spin-wave contributions to the specific heat of these two samples from calculations based on Eq. 2, and using stiffness constant [31,30] and unit cell length [32] from previous neutron scattering and x-ray scattering data respectively. As shown by the solid lines in figure 1, the spin wave calculation fits the  $C(H)$  data extremely well with only a single free parameter – a constant offset which accounts for the non-magnetic contributions to the heat capacity.

Figure 2 and 3 show the low temperature  $C(H)$  of single crystals of  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (PSMO) and  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (NSMO). Recent neutron and x-ray scattering experiments [33] have suggested that at low temperatures while the orbital ordering of  $d_{x^2}^2$ - $d_{y^2}^2$  leads to A-type AFM state in PSMO with no clear evidence for a charge ordering,  $d_{z^2}$  orbitals order in NSMO resulting in a CE-type  $(\pi, 0, \pi)$  type charge ordered AFM state. However, PSMO undergoes a sharp rise in resistivity with an accompanying drop in magnetization, which is usually associated with charge-ordering. At moderate fields the low temperature  $C(H)$  of both PSMO and NSMO increases monotonically with increasing field in contrast to the FM samples, but consistent with the expectations for the AFM materials. The low temperature  $C(H)$  of PSMO (figure 2) increases monotonically with field at low fields due to the softening of the stiffness constant in the AFM state. However, in the region ( $4 \text{ T} \lesssim H \lesssim 8 \text{ T}$ ),  $C(H)$  has a reduced slope, suggesting that the AFM  $\rightarrow$  FM transition which occurs at  $\sim 5 \text{ T}$  [2] is not completed until  $H \sim 8 \text{ T}$ . At higher fields ( $H \gtrsim 8 \text{ T}$ ), in contrast to NSMO (see below) we believe that the change in  $C(H)$  with field is electronic in nature, and the steep rise in  $C(H)$  with increasing field, which coincides with the sharp drop in  $\rho(H)$  is due to

the enhancement of the free carriers as the FM state is percolated throughout the sample. This sample also shows some non-equilibrium effects, e.g.,  $C(H)$  increases by 8 % in  $\sim 10$  mins immediately after the field is raised to 9 T, even when the external parameters, such as temperature and the field remained unchanged. This kind of non-equilibrium behaviour is much more pronounced in the sample which shows strong evidence of a coexistence of FM and charge-ordered state, as discussed below. The gradual relaxation of the FM state in this sample is also possibly responsible for the smaller  $C(H)$  (by  $\sim 10\%$ ) at low fields during subsequent field sweeps.

The low temperature specific heat of NSMO is an order of magnitude higher than the rest of the measured manganites, this is possibly associated with Schottky-like anomaly connected with the large magnetic moment ( $J = 9/2$ ) of the  $\text{Nd}^{3+}$  ion [27,34]. The low temperature  $C(H)$  of NSMO increases monotonically with field at  $H \lesssim 7$  T, demonstrating a stable [33,35] AFM state. At  $H \gtrsim 7$  T, the slope of  $C(H)$  changes, and  $C(H)$  displays a sharp downward turn (see figure 3), suggesting the suppression of thermal excitation of the spin-waves as the sample approaches an  $\text{AFM} \rightarrow \text{FM}$  transition. During subsequent field sweeps  $M(H)$  shows no hysteresis, although  $\rho(H)$  remains order of magnitude smaller, indicating that the carriers remain delocalized even when the field is removed. Since  $C(H)$  shows no hysteresis despite the increase in the population of free carriers [21], this further suggests that the magnetic-contribution dominates the low temperature heat capacity.

Figure 4 shows the low temperature  $C(H)$  of  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ . This sample exhibits all the features of an ACO ground state, with magnetization reaching only  $\sim 2$  % of the total saturation magnetization even at  $H = 7$  T. However, the behaviour of  $C(H)$  is quite different from the other AFM CO samples we studied. The low temperature  $C(H)$  of this sample exhibits features which are rather inconsistent with the thermodynamical expectations for an AFM state, i.e,  $C(H)$  decreases monotonically with increasing field, although the slope of  $C(H)$  is not as sharp as that of the FMM samples. However, when the field is increased from 0 to 9 T,  $C(H)$  drops by only 3.5 mJ. The absolute magnitude of this change is at least a factor of 3 smaller than that of the other measured AFM samples, but quantitatively and

qualitatively similar to the equilibrium  $C(H)$  of the phase-separated samples, as discussed below. This uncharacteristic behaviour of  $C(H)$  in the AFM state can not be attributed to the magnetic excitations, and is perhaps associated with charge/orbital ordering of the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  compounds.

Figure 5 and 6 show low temperature  $C(H)$  of polycrystalline sample of  $\text{La}_{0.50}\text{Ca}_{0.5}\text{MnO}_3$  ( $\text{Mn}^{4+}\% = 53.8$ ) and  $\text{La}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$  ( $\text{Mn}^{4+}\% = 58.2$ ) with well characterized  $\text{Mn}^{4+}$  content. These samples show strong evidence of phase separation into FMM and insulating ACO states [11–21]. The charge-ordered state of the sample with  $x = 0.50$  can be partially dissociated by a moderate external magnetic field, greatly reducing the resistivity, but the sample with  $x = 0.55$  remains largely charge-ordered showing very little magnetoresistance even at  $H = 9$  T.

We find that the behaviour of  $C(H)$  in the phase-separated samples is more complex than the others we have studied, displaying significant non-equilibrium effects. The low temperature zero-field cooled  $C(H)$  of  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  decreases with increasing field, when the field is swept for the first time from  $H = 0 \rightarrow 9$  T. After reaching 9 T, however,  $C(H)$  increases by  $\sim 19\%$  in  $\sim 10$  mins even when field is kept constant at 9 T. On decreasing the field,  $C(H)$  not only remains 17% higher than the initial sweep but is almost constant for  $H \gtrsim 3$  T. However, at lower fields,  $C(H)$  drops sharply at  $H \sim 3$  T with a minimum at  $H \sim 1$  T, and then recovers to near its maximum value at  $H \sim -1$  T. Although the low temperature  $C(H)$  changes by only  $\lesssim 3\%$  on increasing the field in the reverse direction for  $H \gtrsim -6$  T,  $C(H)$  drops sharply at  $H \sim -6$  T, and similar features to those of the initial sweep are observed for  $H \lesssim -6$  T and also during subsequent field sweep from  $H = -9$  T  $\rightarrow 9$  T. To characterize equilibrium behaviour of  $C(H)$ , we also performed the same measurements in an equilibrium mode, i.e., data were taken after waiting for 1 hour at every field, ensuring that the system had reached equilibrium at that field by monitoring  $C$  as a function of time at every field. We observe that the data taken in this equilibrium mode displays only  $\sim 2\%$  rise in  $C(H)$  at  $H \lesssim 3$  T, but at higher fields remains almost flat up to 9 T.

The sharp rise in  $C$  after the field is first swept to 9 T suggests that the FM regimes

are growing with time at the expense of the ACO phase. This increase in  $C$  could then be attributable to an increased population of free carriers or as the enhancement of long wavelength low energy spin-wave excitations with the percolation of the small FM regimes. The minima we observe in  $C(H)$  at  $\sim 1$  T when sweeping the field could similarly be explained by the gradual domain formation or a time-dependent increase in the fraction of the sample which is phase separated into the ACO phase. That  $C(H)$  measured in equilibrium changes very little with field is consistent with behaviour of the  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  sample. This suggests that the magnetic heat capacity of the CO state in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  is much smaller than that of the other ACO samples studied. This is perhaps due to the microscopic phase-separation which inhibits the formation of long wavelength spin modes in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  systems [36].

The charge-lattice of  $\text{La}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$  remains primarily intact even at  $H \sim 9$  T. Although magnetization reveals the presence of small clusters of ferromagnetism, which undergo a first order transition to charge-ordering at a lower temperature than the bulk of the sample, a FM state is not established throughout the sample even at  $H = 9$  T [21]. On increasing the field, the low temperature  $C(H)$  increases by 7% but  $C(H)$  displays a small downward turn at  $H \sim 4$  T before finally dropping sharply at  $H \sim 6$  T. After reaching 9 T,  $C(H)$  rises by 26% in  $\sim 10$  minutes even when the external parameters remained unchanged. Similar features are also observed during subsequent field sweeps though  $C(H)$  shows no non-equilibrium effect. The non-equilibrium effects appear to be intrinsic to the samples which display a coexistence of small clusters of ferromagnetism in the primarily charge-ordered regime, although the extent of this effect decreases for samples far from  $x = 0.50$ .

One other anomalous feature of the heat capacity of the  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  sample is that the magnitude of  $C(H=0)$  is much larger than that of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  or  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ . In fact the enhancement of heat capacity at  $x = 0.50$  has been previously noted, and was suggested to be due to an extra contribution to  $C$  by orbital excitations of the  $d_{z^2}$  orbital ordering [25]. Since we have available samples of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  for a wide range of  $x$  [21],

we also studied this phenomenon briefly with the results plotted in figure 7. We see that there is a sharp rise in  $C(x)$  for  $x = 0.5$  with some scatter around the maximum. This scatter is greatly reduced, however when the data are plotted as a function of the actual  $Mn^{4+}$  content of the samples (as determined by redox titration). This maximum appears to be associated with the doping-induced metal-insulator transition at  $x \sim 0.50$ , and since it is not reflected in the field-dependence of the heat capacity, and since the lattice properties of these materials are quite similar. We hypothesize that the enhancement of  $C(x)$  near  $x = 0.50$  [37–41] is associated with an enhancement of the electron mass near the MIT, but there is no detailed theory to support this possibility.

In conclusion, we have measured low temperature field dependent specific heat of a range of rare earth manganites. Our data suggest that the behaviour of  $C(H)$  is dominated by the magnetic contributions to the specific heat regardless of the nature of the magnetic or electronic state of these materials. Moreover, we observed that the slope of  $C(H)$  with respect to the field for both ferromagnetic and antiferromagnetic samples is typically consistent with the thermodynamic expectations. We also observed that  $C(H)$  of compounds which exhibit evidence of a coexistence of ferromagnetic metallic and antiferromagnetic charge-ordered states show some unusual non-equilibrium effects presumably associated with the phase-separation of the two states.

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## FIGURES

FIG. 1. The specific heat of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  as a function of field at  $T = 5.5$  K, when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9$  T  $\rightarrow$   $-9$  T (solid lines) and  $-9$  T  $\rightarrow$   $9$  T (dashed line). The thick solid line is based on calculation using Eq. 2, as explained in the text. A constant offset is added to the calculated value to account for the non-magnetic contributions to  $C(H)$ .

FIG. 2. The specific heat of  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  at  $T = 5.5$  K as a function of field. All the measurements were done when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9$  T  $\rightarrow$   $-9$  T (solid lines) and  $-9$  T  $\rightarrow$   $9$  T (dashed line). The top and the bottom panel of the inset show resistivity and magnetization at  $T = 5$  K as a function of field.

FIG. 3. The specific heat of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  at  $T = 5.5$  K as a function of field. All the measurements were done when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9$  T  $\rightarrow$   $-9$  T (solid lines) and  $-9$  T  $\rightarrow$   $9$  T (dashed line). The top and the bottom panels of the inset show resistivity and magnetization at  $T = 5$  K as a function of field.

FIG. 4. The specific heat of  $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$  as a function of field at  $T = 5.5$  K, when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9$  T  $\rightarrow$   $-9$  T (solid lines) and  $-9$  T  $\rightarrow$   $9$  T (dashed line).

FIG. 5. The specific heat of  $\text{La}_{0.50}\text{Ca}_{0.50}\text{MnO}_3$  as a function of field at  $T = 5.5$  K, when the sample was measured in continuous mode, when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9$  T  $\rightarrow$   $-9$  T (solid lines) and  $-9$  T  $\rightarrow$   $9$  T (dashed line), and at equilibrium (increasing the field (solid down triangles) and decreasing the field (solid up triangles)) as discussed in the text. The left and right panels of the inset show resistivity ( $M\Omega$  cm) and magnetization at  $T = 50$  K and  $T = 5$  K respectively as a function of field.

FIG. 6. The specific heat of  $\text{La}_{0.45}\text{Ca}_{0.55}\text{MnO}_3$  as a function of field at  $T = 5.5$  K, when the field was swept from  $0 \rightarrow 9$  T (open circles),  $9 \text{ T} \rightarrow -9 \text{ T}$  (solid lines) and  $-9 \text{ T} \rightarrow 9 \text{ T}$  (dashed line). The inset illustrates the field dependent magnetization at  $T = 5$  K.

FIG. 7. The specific heat at  $H = 0$  of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  as a function of Ca doping and measured  $\text{Mn}^{4+}$  content at  $T = 5.5$  K. The large stars illustrate the data from previous measurements from [22,25].